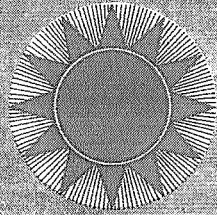


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Development of Lithium Diffused  
Radiation Resistant Solar Cells

First Quarterly Report

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## SUMMARY

The problems associated with diffusion using a  $\text{BBr}_3$  source in an inert ambient were reviewed. The problems included: 1) inconsistent results with respect to both the visual appearance and sheet resistance measurements of cell blanks from one diffusion to the next; 2) nonuniformity in the electrical characteristics as the number of cells per diffusion was increased above ten; and 3) rapid depletion of the liquid source in the bubbler and, consequently, increased cost for the source. A decision was made to investigate the potential of using a modified  $\text{BCl}_3$  diffusion source process both with and without  $\text{O}_2$ , since of the three problems mentioned above, the second is the only one which is also a problem with  $\text{BCl}_3$  diffusions as they are presently done.

Varying the boron deposition time in the standard  $\text{BCl}_3$  diffusion without  $\text{O}_2$  showed that the stresses were reduced with shorter deposition times; 2x6 cm cells as thin as 0.006" were successfully diffused with no bowing.

Use of  $\text{O}_2$  with the  $\text{BCl}_3$  was also investigated. In this process the  $\text{BCl}_3$  reacts with  $\text{O}_2$  to form  $\text{B}_2\text{O}_3$  which deposits on the silicon blank as a glass layer. This diffusion, if successfully optimized, should reproduce the low stress cells obtained with shorter deposition times in the standard  $\text{BCl}_3$  diffusion, as well as meet the requirements of special cell types for a non-etching diffusion source. So far, this diffusion has produced cells (1 ohm cm base resistivity) with outputs higher than 30 mW, which is equivalent to better than 11.3% efficiency. This is only 4 to 5% lower than typical efficiencies of cells diffused with the standard  $\text{BCl}_3$  diffusion (no  $\text{O}_2$ ). Reproducibility with respect to visual appearance, sheet resistance, and electrical output, though dependent upon the location of the cell blanks in the diffusion zone as well as their vertical or horizontal placement on the diffusion boat, was good from one diffusion to the

next. Measurement of cell thickness before and after diffusion indicated that no silicon was etched and diffusion of 2x6 cm blanks with no bowing indicated relatively low stresses. The results of both of these two new boron diffusion processes appear very promising and both should have more potential for use in production.

Crucible grown P/N solar cells which have been lithium diffused eight hours at 325°C have exhibited typical efficiencies of about 10.5% with a range from 9.8 to 11.8%. Fabricating more than two hundred of these cells has made it clear that these diffusion parameters produce good high output lithium cells; however, two problems peculiar to these particular parameters have been observed; 1) a soft knee characteristic and 2) excess current at small forward and reverse biases.

The soft knee reduces the cell output and open circuit voltage between 2 and 15%. In more than 90% of the cells exhibiting the effect, it has been eliminated by etching the cell edges.

High currents at low forward and reverse bias can be caused by tunneling or Zener breakdown which is characterized by a soft reverse characteristic. The breakdown voltage is low and ill-defined. High fields, which are present with narrow P-N junctions and which have been proposed to occur at localized points due to metal precipitates, are a prerequisite for tunneling. Reverse biasing cells (lithium diffused eight hours at 325°C) to 10 volts in the dark showed that tunneling was indeed occurring. Measurement of 1 ohm cm P/N cells with no lithium, and lithium cells with diffusion parameters other than eight hours at 325°C showed that the majority of these cells also exhibited some degree of tunneling. However, only the lithium cells diffused eight hours at 325°C showed excessively high current between 0 and 0.1 volt in the reverse direction and a shunted characteristic in the forward direction when illuminated. The reason for this correlation of tunneling to the eight hour 325°C diffusion is not yet clear, however, some experiments are planned where the diffusion times at 325°C will be varied and this may help clarify this effect.

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INTRODUCTION

The goal of this contract is to investigate the effect of various process parameters on lithium doped solar cell performance. This program is a continuation of work done on JPL Contract 952547-Part I, and has been organized into five areas of study. The five basic areas include: P-N diffusion studies, material studies, lithium diffusion studies, special structure studies and contact studies.

The purpose of the P-N diffusion studies is to develop a boron diffusion which: 1) does not etch silicon, 2) will yield higher efficiency lithium cells due to reduced stresses and 3) can be used for larger area and thinner cells (also due to reduced stresses).

As part of the material studies, parameters such as oxygen content of crucible grown silicon will be investigated.

Lithium diffusion investigation will be performed in the following areas:

- 1) Diffusion profiles as a function of cell thickness for various diffusion times and temperatures will be analyzed.
- 2) Additional cells with lithium diffusions of eight hours at 325°C will be fabricated and studied to verify that the extremely high initial and recovered outputs can be made reproducibly with high yields.
- 3) The diffusion time at 325°C will be varied since eight hours does not seem to be optimum for float zone silicon.

- 4) Lithium evaporations will be investigated further in order to optimize the procedure and determine on a statistical basis cell output as a function of lithium application.

In the contact studies the performance of TiAg contacts on lithium cells in typical specification acceptance and qualification tests will be evaluated. The tests will include humidity testing of soldered cells, pull test before and after humidity tests, temperature cycling, and evaluation of the effects of soldering and interconnecting on cell performance.

In addition to the experimental studies, 600 lithium doped solar cells will be fabricated for radiation testing and analysis by JPL.

During this quarter  $\text{BCl}_3$  diffusions both with and without  $\text{O}_2$  were investigated. Also, two characteristics, a soft knee and excess current at low forward and reverse biases, observed in lithium cells diffused eight hours at  $325^\circ\text{C}$  were studied.

## 2.0 TECHNICAL DISCUSSION

### 2.1 BORON DIFFUSION EXPERIMENTS

Early in this quarter, the problems associated with the  $\text{BBr}_3$  diffusion in an inert ambient were reviewed. These problems included: (1) inconsistent results with respect to both the visual appearance and sheet resistance measurements of cell blanks from one diffusion to the next; (2) nonuniformity in the electrical characteristics as the number of cells per diffusion was increased above ten; and (3) rapid depletion of the liquid source in the bubbler which represents an appreciable cost for the source.

Relatively stress-free cells (both thin and large area cells have been diffused with no bowing) with efficiencies of 11% (generally about 5% lower than the output of  $\text{BCl}_3$  diffused cells) have been fabricated using the  $\text{BBr}_3$  source. In spite of these promising results a decision was made to investigate several modifications to the  $\text{BCl}_3$  process, since of the three problems mentioned above which are encountered with the present  $\text{BBr}_3$  diffusion process, the second is the only one which is a problem with the  $\text{BCl}_3$  diffusion. It was postulated that the etching reaction associated with the  $\text{BCl}_3$  process could be minimized or eliminated by having oxygen present to form a non-etching glassy boron source layer. Alternatively, it was postulated that the etching reaction might be minimized by simply reducing the amount of  $\text{BCl}_3$  present. It was hoped that these modifications would be able to duplicate the present state-of-the-art  $\text{BBr}_3$  diffusion with respect to producing relatively stress-free thin and large area cells without the problems which are being encountered with the  $\text{BBr}_3$  diffusion.

Therefore, the boron diffusion investigation performed this quarter included experiments to determine the feasibility of using a modification of the present  $\text{BCl}_3$  diffusion (without  $\text{O}_2$ ) to produce unbowed thin and large area blanks as well as experiments using oxygen with the  $\text{BCl}_3$ , which if successful, should not only take care of the stress problem but also the requirement with special cell types of a non-etching diffusion source.

### 2.1.1 BCl<sub>3</sub> Diffusions without O<sub>2</sub>

In order to determine whether the BCl<sub>3</sub> diffusion process as it was carried out without oxygen could be optimized for diffusion of either thin cells or large area cells, an experiment was performed in which the boron deposition time was varied. The standard BCl<sub>3</sub> diffusion was performed with an 8 minute warm-up, an 8 minute deposition, and a 10 minute drive-in time. In this experiment the source deposition time was varied from 8 minutes down to 2 minutes. It was found that the sheet resistance which ranged from 16.3 to 17.9 ohms/square did not change with the boron deposition time. Even the 2 minute deposition time resulted in a boron layer sufficient to produce an infinite source and a good boron diffusion with measured sheet resistances of 16.3 and 17.1 ohms/square. Four out of eleven cells diffused with a 2 minute deposition had exceptionally good electrical characteristics with outputs ranging from 31.0 to 33.2 mW and fill factors of 0.752 to 0.765; however, seven of the cells had fill factors less than 0.75 (ranging from 0.684 to 0.746) and correspondingly lower outputs. The low fill factors were not confined to cells in the 8-2-10 diffusion, but there was a higher percentage of these poorer curve shape cells from the 8-2-10 diffusion. The average short circuit currents of the cells diffused with 2 and 8 minute deposition times were 69.7 and 70.6 mA, respectively, a difference of only 0.9 mA. At 500 mV the difference in current for the two different deposition times was approximately 6 mA. In the diffusions with the shorter deposition times the rounded knee or low fill factor is believed to be caused by insufficient etching of the cell surface, resulting in incomplete removal of surface damage.

Figure 1 compares the best output cells from each diffusion (see also Table 1). The best cell with an 8 minute boron deposition time has an output of 35.5 mW (measured at 25°C in a solar simulator at 140 mW/cm<sup>2</sup>), a short circuit current of 71.9 mA, an open circuit voltage of 626 mV,

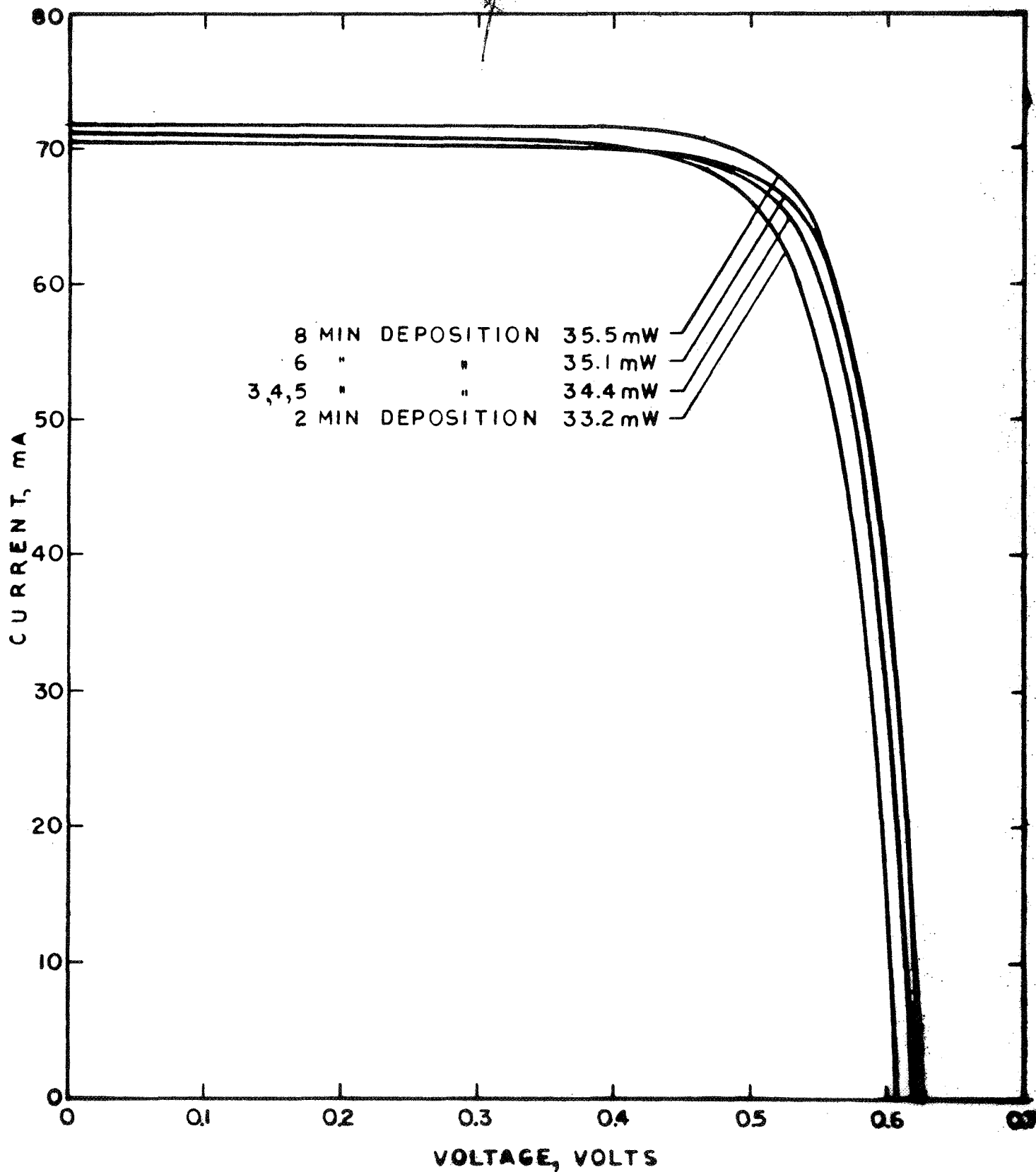


Figure 1. Best Output Cells from  $BCl_3$  Diffusions with Different Deposition Times. 1 ohm cm crucible grown P/N cells; measured in solar simulator at  $140 \text{ mW/cm}^2$  and  $25^\circ\text{C}$ .

Table 1  
Electrical Characteristics of High Output P/N Cells  
from Experiment Investigating Boron Deposition Time

Deposition Time, min	$I_{sc}$ , mA	$V_{oc}$ , mV	Fill Factor	$P_{max}$ , mW	Efficiency, %
8	71.8	626	.790	35.5	13.1
6	70.5	624	.795	35.1	12.9
3, 4, 5	70.5	621	.786	34.4	12.7
2	71.2	609	.765	33.2	12.2

and a fill factor of 0.790. The best cell with a 2 minute boron deposition had a lower short circuit current, 71.1 mA, and open circuit voltage, 609 mV; but even with these lower values for short circuit current and open circuit voltage, the output was 33.2 mW.

In another experiment a 2 minute boron deposition time was used for a diffusion which included 0.004, 0.014 and 0.017 inch thick 1x2 cm blanks and 0.006 and 0.014 inch thick 2x6 cm blanks. Figure 2 shows the placement of the cells on the boat. The 0.004 inch thick 1x2 cm blanks were placed at each end of the boat to check for bowing effects. The 2x6 cm blanks were placed in the center and the 0.014 and 0.017 inch thick 1x2 cm blanks were placed on both sides of the 2x6 cm blanks. The 0.004" blanks at the front of the boat (with respect to the gas flow) were bowed, while those at the back were not. The 0.014 and 0.017" 1x2 cm blanks as well as the 0.006 and 0.014" 2x6 cm blanks were not bowed. This experiment showed that  $BCl_3$  like  $BBr_3$ , can be used in an oxygen-free ambient to produce relatively stress-free thin and large area boron diffused cells.

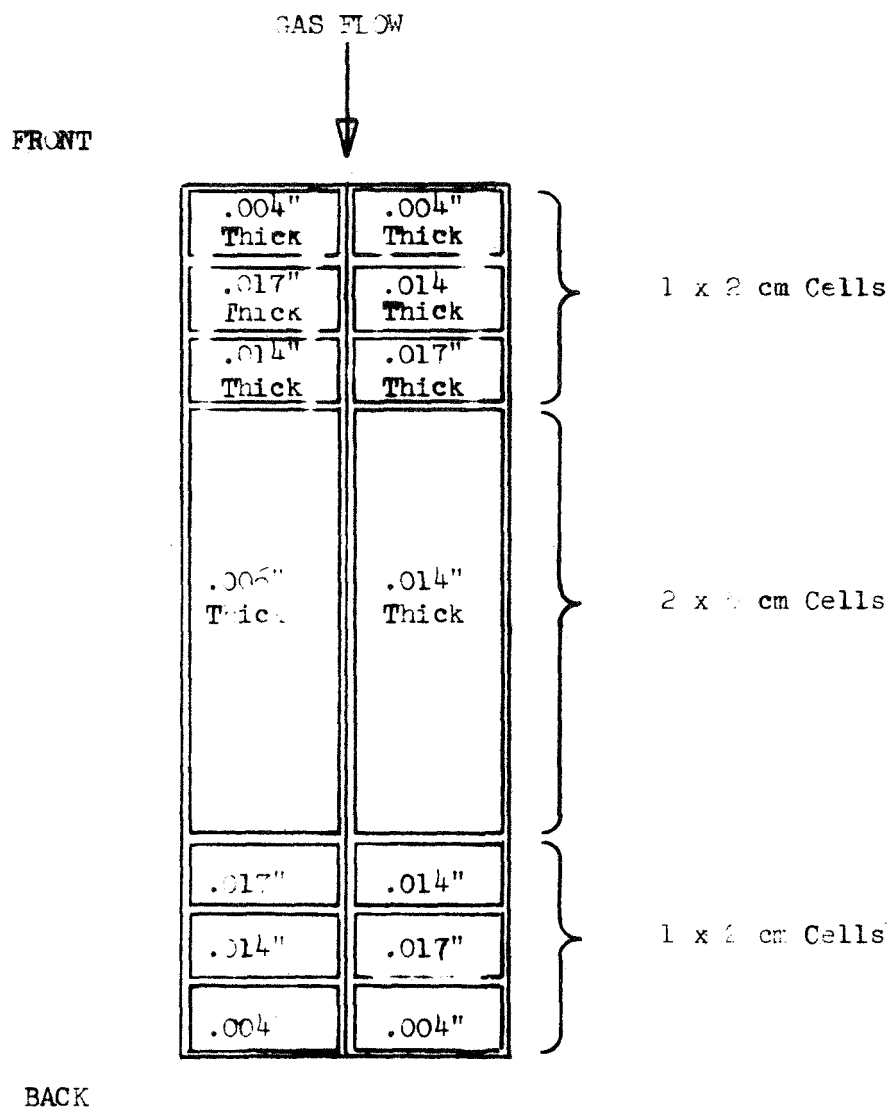


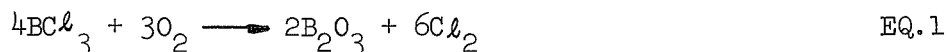
Figure 2. Cell Placement on Diffusion Boat to Check for Stresses in  $\text{BCl}_3$  Diffusion.

### 2.2.2 BCl<sub>3</sub> Diffusions with O<sub>2</sub>

A schematic of the BCl<sub>3</sub> system with O<sub>2</sub> added to the ambient gas is illustrated in Figure 3. The individual steps in this modified boron diffusion process are given below.

1. Cell blank warmup - cell blanks are allowed to reach thermal equilibrium. Only N<sub>2</sub> gas is flowing during this part of the cycle.
2. Deposition of source - the BCl<sub>3</sub> reacts with O<sub>2</sub> to provide the local source (B<sub>2</sub>O<sub>3</sub>) which deposits as a glass layer on the cell blanks. BCl<sub>3</sub>, O<sub>2</sub> and N<sub>2</sub> gases are used.
3. Drive-in - the boron in the deposited glass layer diffuses into the surface of the cell blanks. N<sub>2</sub> gas is flowing in this part of the cycle to remove any remaining reactants in the diffusion tube.

The reaction of BCl<sub>3</sub> with O<sub>2</sub> produces the local impurity source, B<sub>2</sub>O<sub>3</sub>, according to the reaction,



and then B<sub>2</sub>O<sub>3</sub> may react with silicon,



A third reaction that also may occur is that of silicon with O<sub>2</sub>,



In order to determine if these reactions do take place at the temperature of diffusion (1055°C) and to what extent they proceed to completion, thermodynamic values of the free energy reaction isotherm and equilibrium constants were examined.

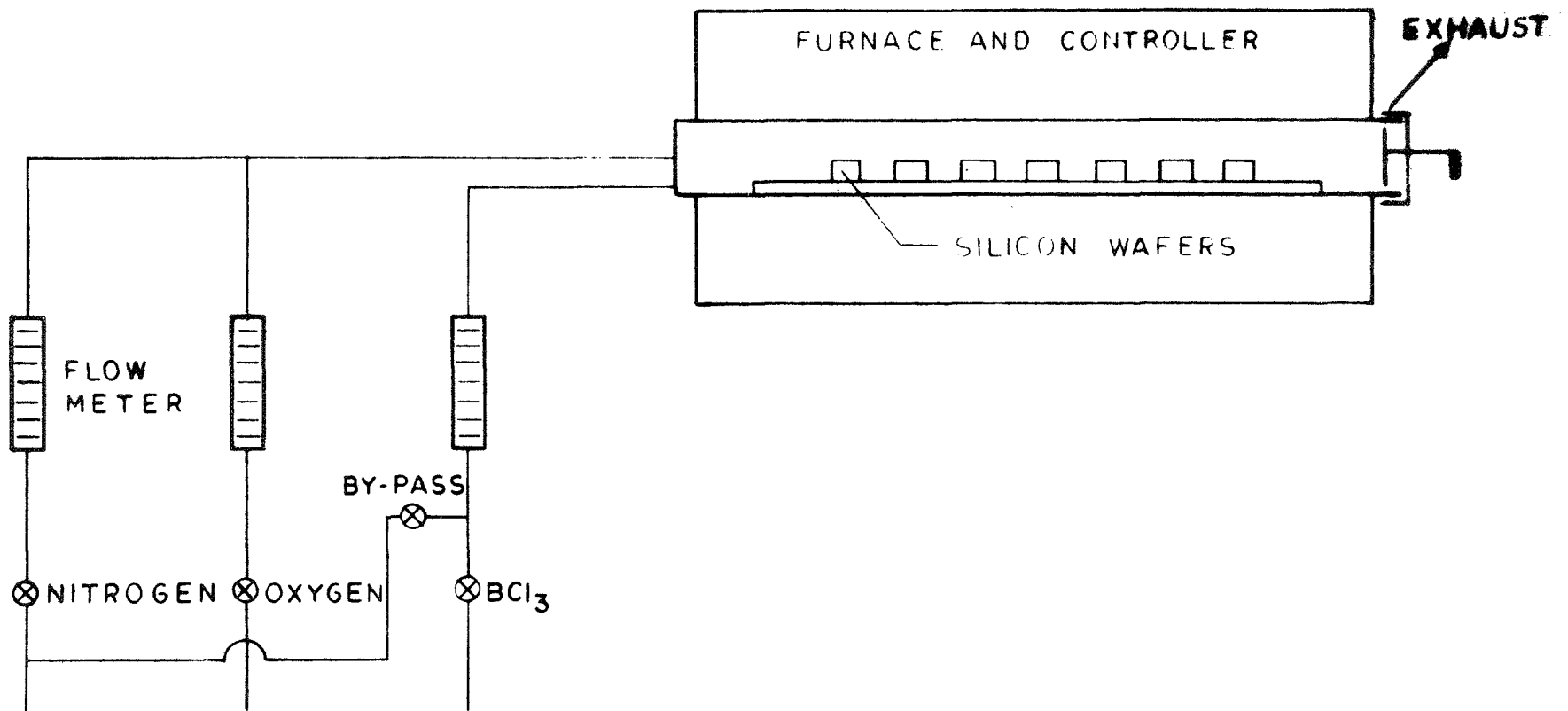


Figure 3. Elementary Diffusion System Using a Gaseous Impurity Source.

The standard free energy change for a reaction from reactants to products at STP (standard temperature and pressure, 25°C, 1 atm.) is given by,

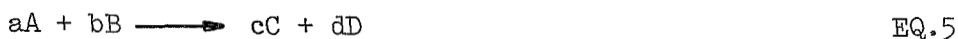
$$\Delta F^{\circ} = -RT \ln K \quad \text{EQ. 4}$$

where:  $R = 1.987$  calories/mole  $^{\circ}\text{K}$  (ideal gas law constant)

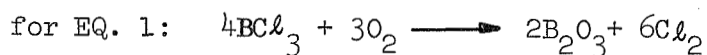
$T =$  temperature ( $^{\circ}\text{K}$ )

$$K = f_C^c f_D^d / f_A^a f_B^b \quad - \text{equilibrium constant}$$

The reactions being considered are of the form,



The equilibrium constant may now be calculated to provide information as to the completeness to which these reactions proceed.



$$\Delta F^{\circ(1)}_{\text{BCl}_3} = -90.9 \text{ Kcal/mole}$$

$$\Delta F^{\circ(1)}_{\text{B}_2\text{O}_3} = -280.4 \text{ Kcal/mole}$$

$$\Delta F^{\circ} = \sum(\Delta F^{\circ} \text{Products}) - \sum(\Delta F^{\circ} \text{Reactants})$$

$$\Delta F^{\circ} = 2(-280.4 \text{ Kcal/mole}) - 4(-90.4 \text{ Kcal/mole})$$

$$\Delta F^{\circ} = -197.2 \text{ Kcal/mole}$$

This computation was similarly applied to equations 2 and 3 with the following results:

$$\Delta F^{\circ}(\text{EQ. 2}) = -16.4 \text{ Kcal/mole}$$

$$\Delta F^{\circ}(\text{EQ. 3}) = -192.4 \text{ Kcal/mole}$$

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(1) Handbook of Chemistry and Physics, 42nd Edition, Chemical Rubber Publishing Co.

Equation 4 may now be used to calculate the equilibrium constants for equations 1, 2 and 3.

$$\text{for EQ.1: } \ln K = \Delta F^0(1)/-RT = \frac{-197.2 \times 10^3 \text{ cal/mole}}{-(1.987 \text{ cal})/(298^\circ\text{K}) \text{ mole } ^\circ\text{K}}$$

$$\therefore \ln K = 333$$

$$\text{for EQ. 2: } \ln K = 27.7$$

$$\text{for EQ. 3: } \ln K = 325$$

From the values of the equilibrium constants obtained through these calculations the free energy reaction isotherm may be calculated from which reaction spontaneity can be predicted according to the relationship,

$$\Delta F = \Delta F^0 + RT \ln K_T \begin{cases} \Delta F < 0, \text{ spontaneous} \\ \Delta F > 0, \text{ nonspontaneous} \end{cases} \quad \text{EQ.6}$$

Since the equilibrium constant of equation 6 is temperature-dependent as given by the van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \text{ or by simple integration,}$$

$$\ln K_T = \ln K_{298^\circ\text{K}} + \frac{\Delta H^0}{R} \left( \frac{1}{298^\circ\text{K}} - \frac{1}{T} \right) \quad \text{EQ.7}$$

Finally it becomes necessary to determine  $\Delta H^0$  (enthalpy) as a function of temperature given by the following expression,

$$H_T^0 - H_{298^\circ\text{K}}^0 = \sum \left[ \int_{298^\circ\text{K}}^T C_p dT(\text{products}) \right] - \sum \left[ \int_{298^\circ\text{K}}^T C_p dT(\text{reactants}) \right] \quad \text{EQ.8}$$

The values of the enthalpy were thus determined for the temperature  $1328^{\circ}\text{K}$ ; these in turn were substituted into equation 7 which provides the values of the equilibrium constant (K) at this temperature. Finally these values of K were substituted in equation 6 and the free energy reaction isotherms ( $\Delta F$ ) were calculated.

As indicated by equation 6, for a reaction to be spontaneous at a particular temperature, the value of  $\Delta F < 0$  must be satisfied. Calculation of  $\Delta F$  for the reactions of equation 1, 2 and 3 were made and all three satisfy this condition. Thus all three reactions can be expected to occur at the temperature used for the diffusion of silicon wafers and proceed to completion.

Using chemically polished cell blanks a group of three diffusions were performed in which the rate of  $\text{O}_2$  flow was varied from 7 to 1400 ml./min. All other system parameters were maintained at the same values for each diffusion in this group. At the high  $\text{O}_2$  flow the resulting cell blanks were left with a multi-colored layer which could not be removed by chemical means which did not etch the silicon. Diffusion with low  $\text{O}_2$  flow rates produced a hard, black deposit on the cells. Since this layer was similar to that obtained in the conventional diffusion using  $\text{BCl}_3$  in an inert ambient, its removal was attempted by similar means, boiling in hot nitric acid. While complete removal by chemical means was unsuccessful, some of this layer flaked off leaving a damaged polished surface. In diffusion at slightly higher  $\text{O}_2$  flow rate (80 ml./min) the cell blanks appeared to have a transparent glass layer. These cell blanks were treated in concentrated  $\text{HF}(49\%)$  and measured for their sheet resistance as well as for the presence of a p-type layer with the hot-point probe.

The criteria used in the selection of diffused cell blanks for solar cell fabrication were taken from the conventional  $\text{BCl}_3$  process, i.e., similar p-type surface concentrations as determined by sheet resistance measurements. Solar cells were then fabricated and the I-V characteristics were measured. Figure 4 compares I-V characteristic curves

(measured in a solar simulator at  $140 \text{ mW/cm}^2$ ,  $25^\circ\text{C}$ ) of a cell diffused by  $\text{BCl}_3$  with  $\text{O}_2$  and a cell diffused by the conventional  $\text{BCl}_3$  process in an inert  $\text{N}_2$  ambient. The cell diffused in  $\text{BCl}_3$  with  $\text{O}_2$  is approximately 2 mA lower at short circuit current and 1.4 mW lower in maximum power; however, the 30.6 mW output is equal to an efficiency of 11.5%. The results of this diffusion process have been reproducible, although the repeatability appears to be dependent on the location of the cell blanks in the diffusion zone as well as their vertical or horizontal placement on the diffusion boat.

To investigate both the amount of silicon etched, and the stress effects, one diffusion was conducted in which the cell blank thicknesses were measured before and after diffusion. The 0.011 to 0.014" thick 2x6 cm cells investigated did not change in thickness nor was any bowing apparent.

While this process appears to be highly successful, a determination of its feasibility for large cell quantities still needs to be made.

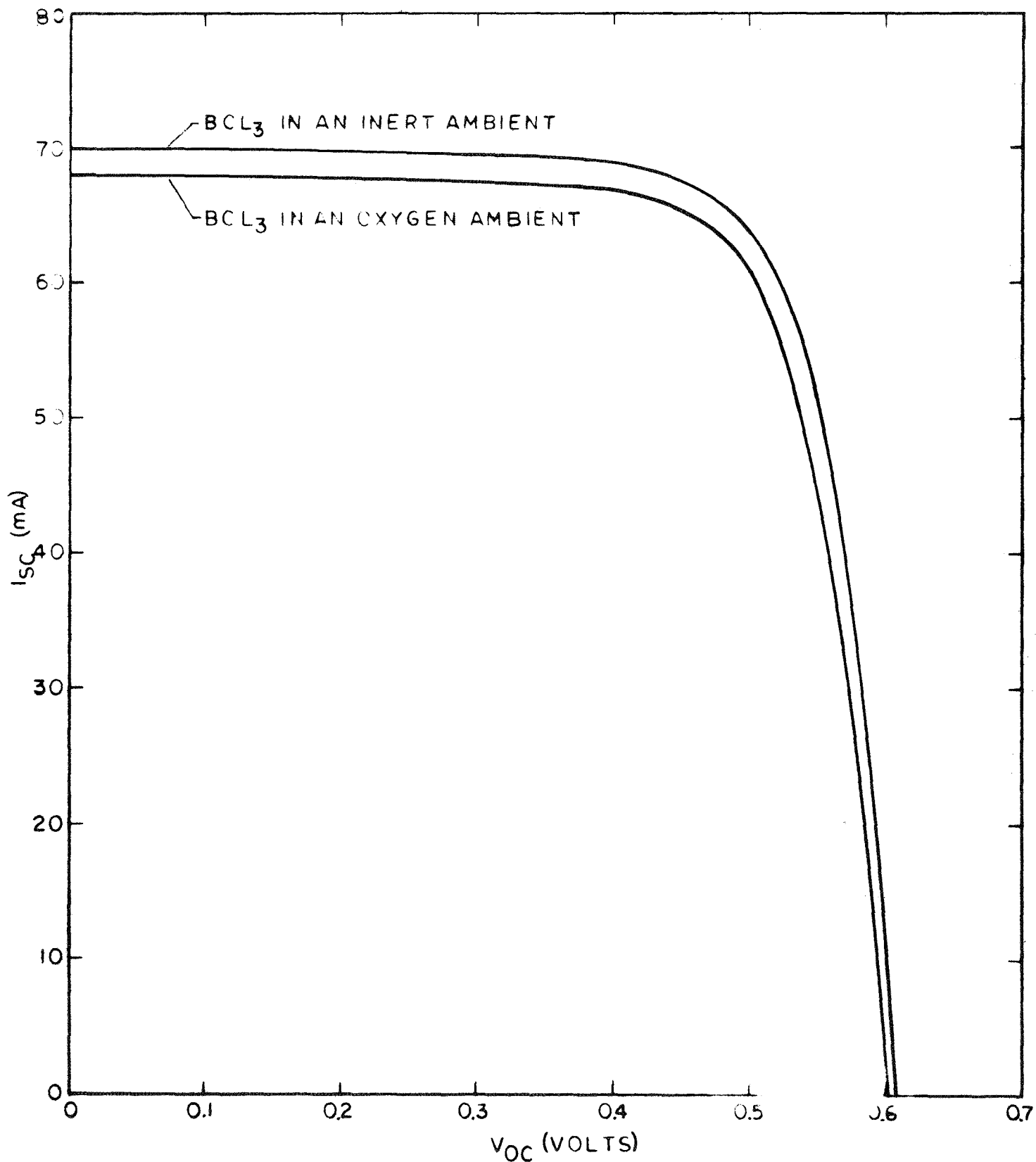


Figure 4. I-V Characteristics of Cells Diffused by Two Different  $BCl_3$  Processes. Measured in solar simulator at  $140 \text{ mW/cm}^2$  and  $25^\circ\text{C}$ .

## 2.2

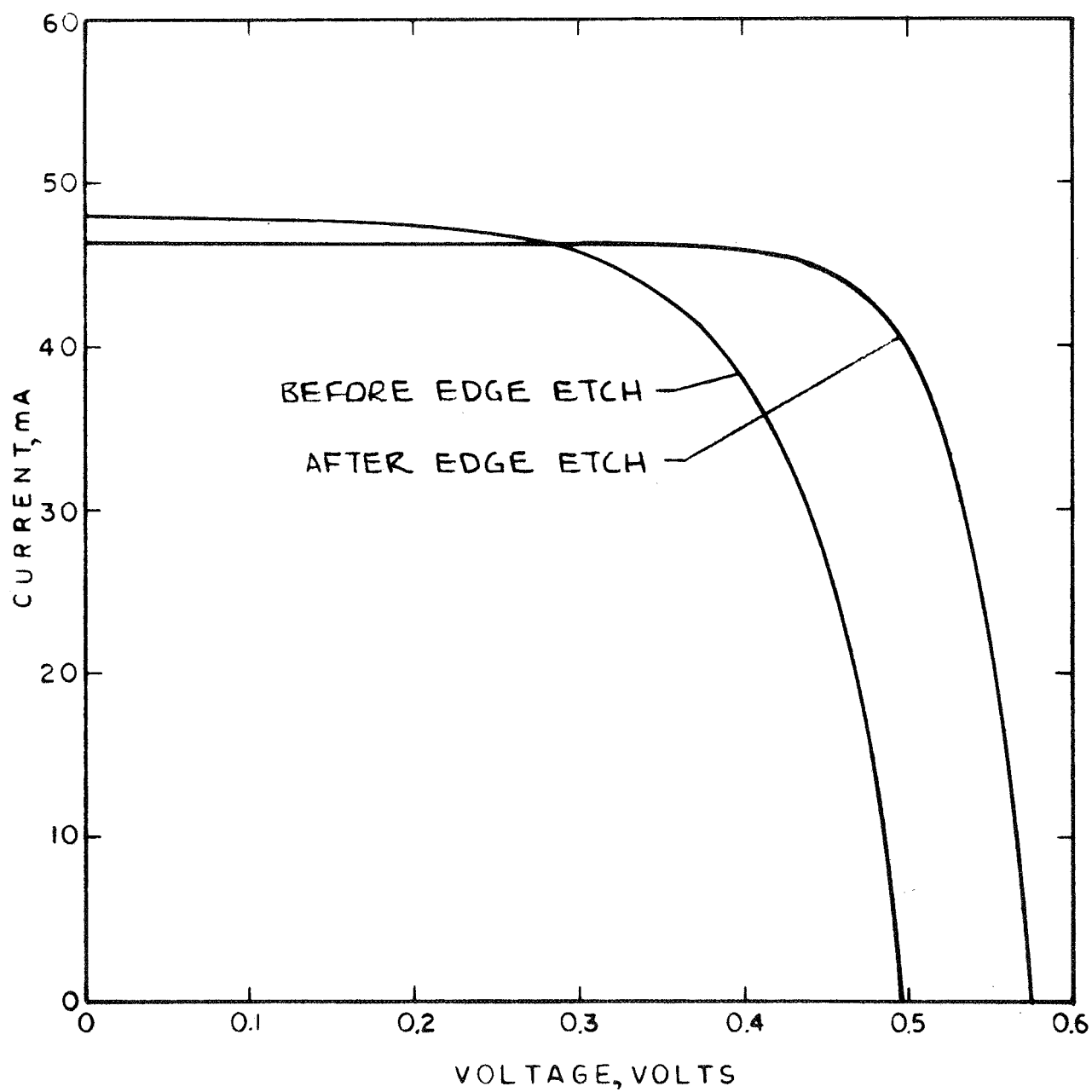
### EIGHT HOUR LITHIUM DIFFUSIONS

More than two hundred crucible grown P/N solar cells with typical efficiencies of about 10.5% and a range from 9.8 to 11.8% have now been fabricated with an eight hour lithium diffusion at 325°C. Fabricating this quantity of cells has made it clear that these diffusion parameters produce very high output lithium cells; however, problems peculiar to these particular parameters have been observed. These problems include a soft knee characteristic and excess current at small forward and reverse biases.

The soft knee characteristic varies and frequently affects the open circuit voltage as well as the knee of the curve. Figure 5 shows a cell (measured in a 100 mW/cm<sup>2</sup> tungsten light source at 25°C) with a soft knee and an open circuit voltage of 498 mV. When the cell was edge etched the short circuit current was reduced by about 1.5 mA, but the open circuit voltage increased from 498 to 575 mV, the maximum power, from 16.1 to 20.4 mW and the curve factor, from 0.67 to 0.77.

Figure 6 shows the effect of edge etching a more typical cell. The soft knee was not as pronounced and the improvement in open circuit voltage with edge etching, 12 mV, was 2% rather than the 15% obtained from the previously described cell. Although the reason for the occurrence of the soft knee in cells lithium diffused eight hours at 325°C has not been determined, it is obviously a surface effect since in over 90% of the cells measured it has been improved by etching the cell edges in an HF - HNO<sub>3</sub> mixture.

The second problem observed with P/N cells which have been lithium diffused 8 hours at 325°C resembles a tunneling or internal field emission effect. In the fourth quadrant portion of the I-V characteristic curve which is typically measured, the effect appears to be caused by high leakage current (Figure 7). When the dark reverse or leakage current was measured, it was found to be only 57.5 μA at 0.7 V (Figure 8), however, the dark reverse characteristic exhibited anomalous behavior in that the current rose rapidly to 38 μA at 0.1 V and then leveled off



**Figure 5.** Effect of Edge Etch on a Lithium Cell Diffused Eight Hours at 325°C. Measured in 100 mW/cm<sup>2</sup> tungsten light source at 25°C.

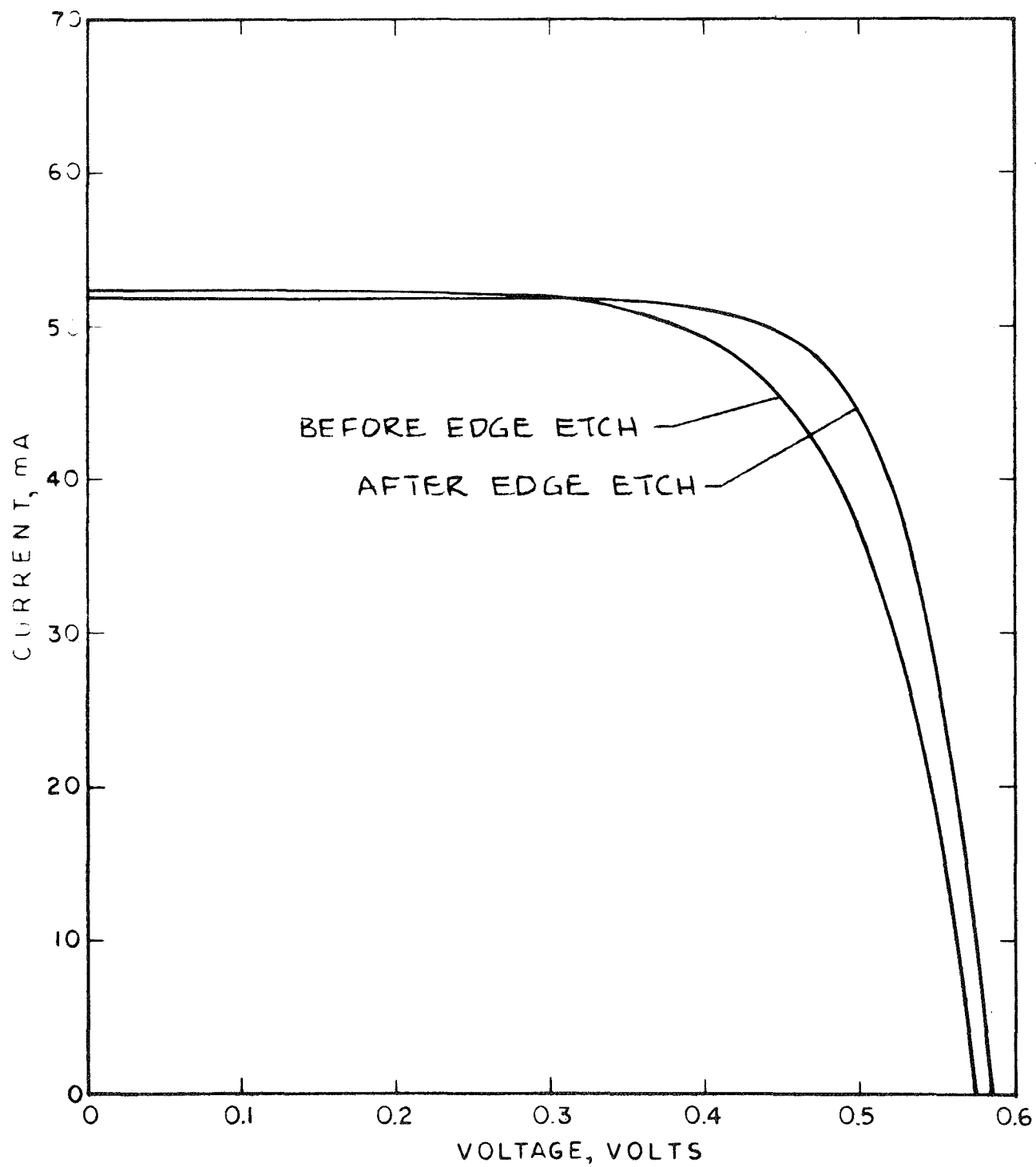


Figure 6. Effect of Edge Etch on a Lithium Cell Diffused Eight Hours at 625°C. Measured in 100 mW/cm<sup>2</sup> tungsten light source at 25°C.

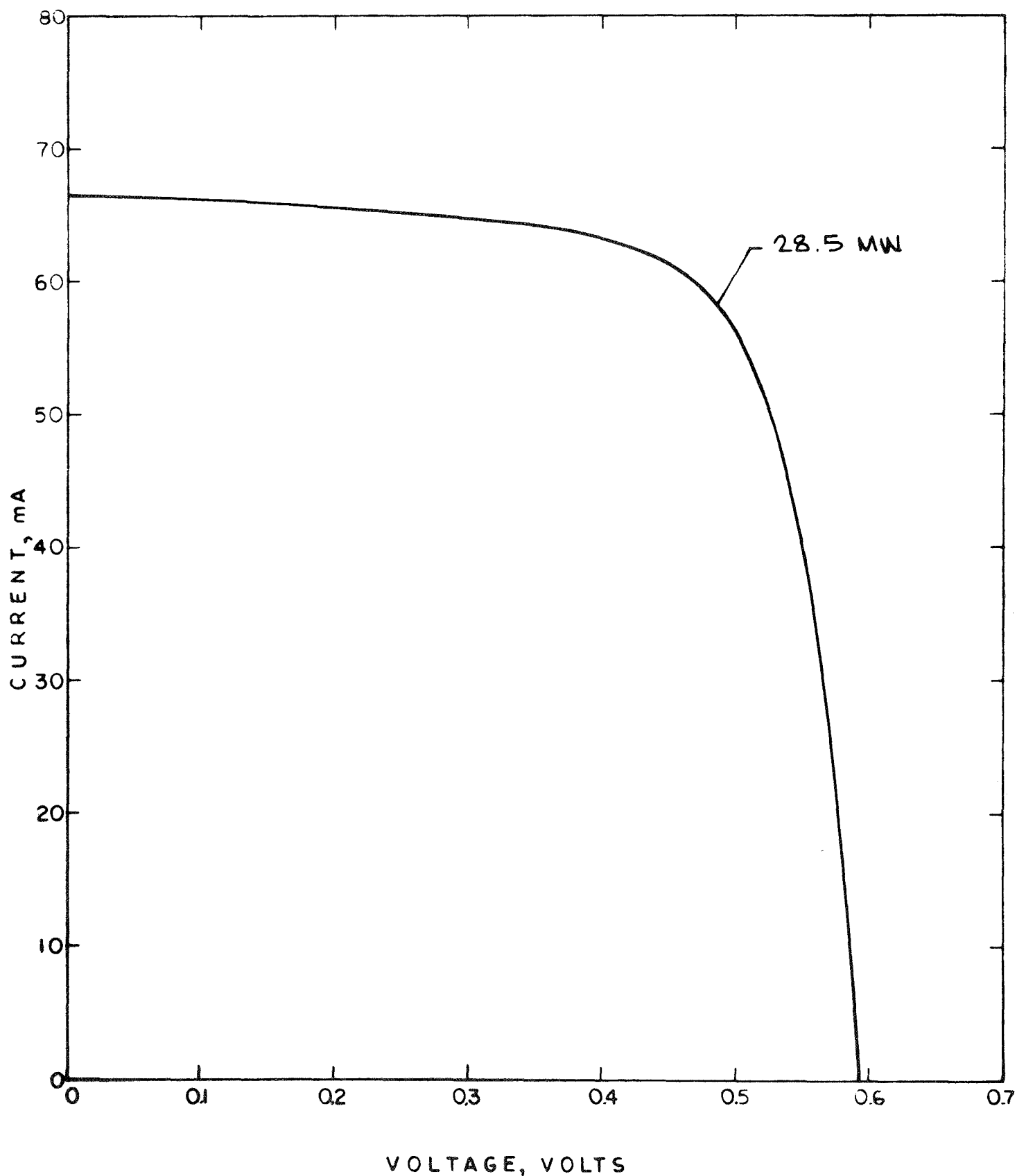


Figure 7. I-V Characteristic Curve of a "Shunted" Crucible Grown P/N Cell (#8745) Lithium Diffused Eight Hours at 325°C. Measured in a solar simulator at 140 mW/cm<sup>2</sup> and 25°C.

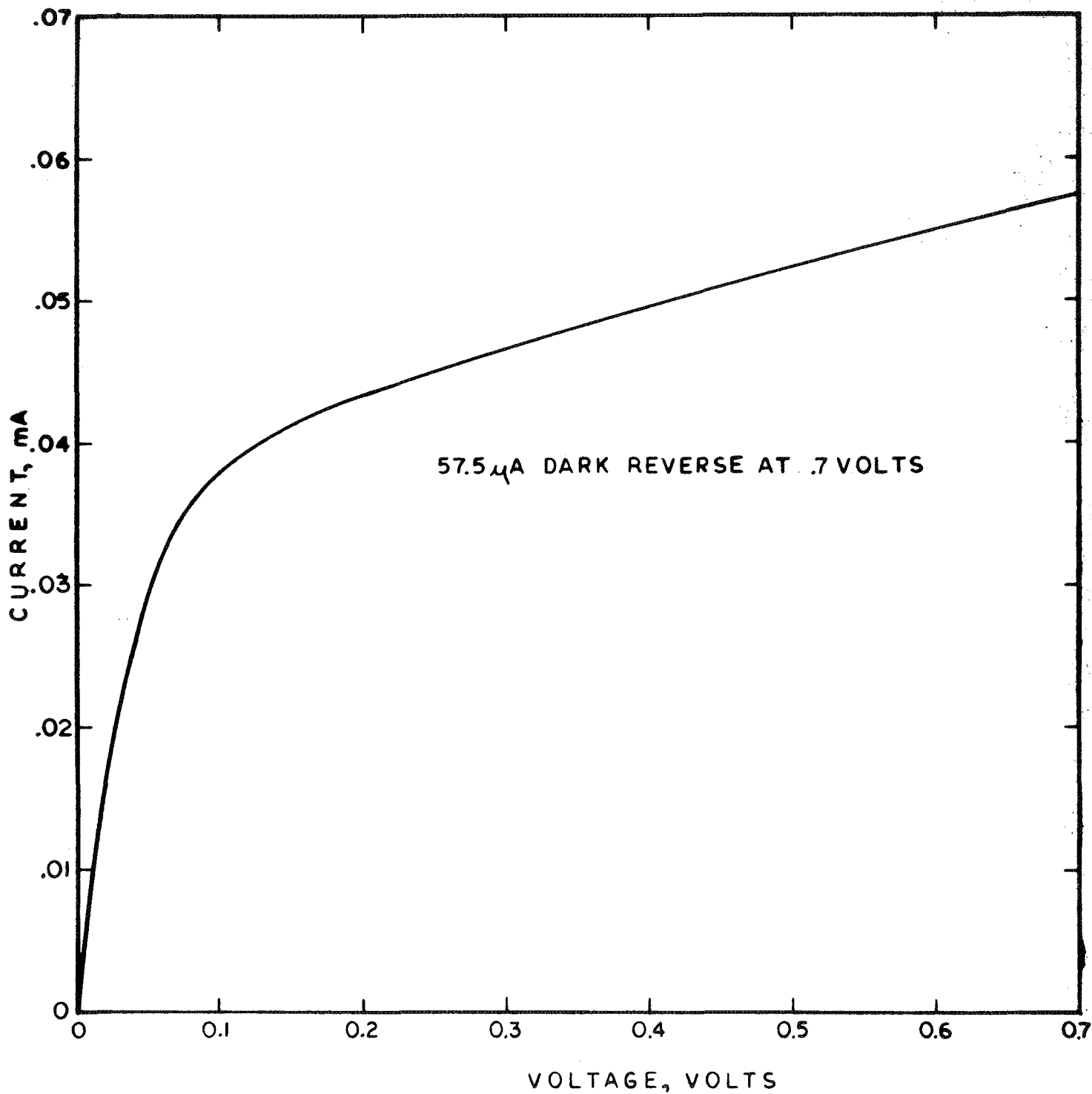


Figure 8. Dark Reverse Characteristic of the Lithium Cell (#8745) Shown in Figure 7.

between 0.1 and 0.7 V. Measurement of the dark forward I-V characteristic also showed high currents at low voltages. In Figure 9 the dark forward I-V characteristic curve of the same cell (#8745) shown in Figures 7 and 8 is compared to a lithium cell which was diffused 90 minutes and redistributed 60 minutes at  $425^{\circ}\text{C}$  (Cell A). The characteristic of Cell A approaches the theoretical linear relationship and between 0.5 and 0.7 V the current of cell #8745 is in the same range; however, below 0.45 V the characteristic of cell #8745 deviates drastically from a linear relationship with the current being one order of magnitude higher at 0.3 V and two orders of magnitude higher at 0.1 V. Internal field emission; ie., tunneling, can account for anomalously high currents at low voltages. With narrow P-N junctions high fields in the space charge region result in considerable internal field emission at very small forward biases.<sup>(2)</sup>

If tunneling is causing high current at low forward and reverse bias in these eight hour lithium diffused cells, it is not due to the same characteristics as those in a tunnel diode in which both the p and n layers are heavily doped ( $>10^{19}$  atoms/cm<sup>3</sup>), or in a backward diode (doping concentrations on the p and n side of the junction are nearly or not quite degenerate) in which the current in the reverse direction for small bias is larger than the current in the forward direction. The lithium cell does not have  $10^{19}$  atoms/cm<sup>3</sup> in the n region nor is the reverse current higher than the forward current at low bias. Since tunneling has been proposed to occur at localized high field points caused by metal precipitates,<sup>(3)</sup> it is quite possible that lithium in the junction region is the cause of the tunneling.

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(2) Chynoweth, A.G. and K.G. McKay, "Internal Field Emission in Silicon P-N Junctions," The Physical Review, Vol. 106, No. 3, p. 423, May, 1957.

(3) Goetzberger, A. and W. Shockley, "Metal Precipitates in Silicon P-N Junctions," Journal of Applied Physics, Vol. 31, p. 1821, 1960

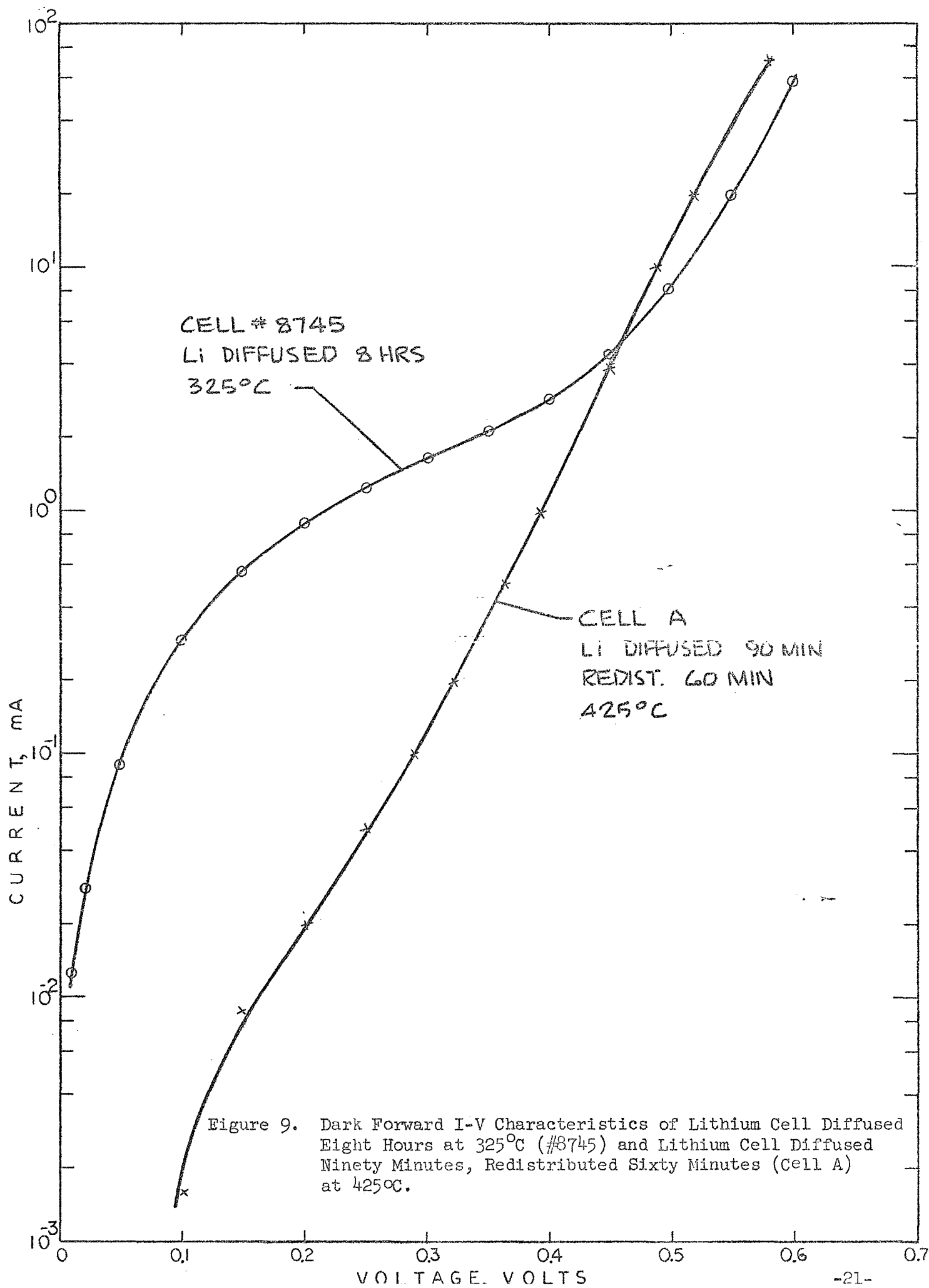


Figure 10 compares a 1 ohm cm crucible grown P/N (no lithium) to the lithium cell #8745. When biased in the reverse direction the 1 ohm cm P/N cell exhibits a constant slope of 10  $\mu$ A/volt until the onset of avalanche breakdown between 5.8 and 5.9 volts. In the lithium cell there is considerable softness in the reverse characteristic, indicative of tunneling or internal field emission. Lithium metal precipitates may be acting as intermediate trapping levels through which a series of tunneling transitions could occur. The reason for the extremely high current flow between 0 and 0.1 V may be that the trapping states conduct high current initially, but then become filled and reach a saturation level. Chynoweth and McKay suggest that if internal field emission occurs from both impurity levels and the valence band, "emission from impurities is an attractive hypothesis in that the reverse current at a particular spot would be prevented from increasing too rapidly with voltage by the rate at which the impurities can be activated. The fact that the forward characteristics indicate field emission still occurring at forward biases of up to 0.4 volt suggests that emission from impurity levels is important."<sup>(4)</sup>

Measurement of additional 1 ohm cm P/N cells with no lithium as well as cells diffused 90 minutes and redistributed 60 or 120 minutes at 425°C indicated that varying degrees of tunneling was occurring in most of the cells; however, the forward current at low voltage was not affected to the same degree nor did the reverse current increase as rapidly between 0 and 0.1 volt. At present it is not clear why internal field emission is more severe with the eight hour diffusion at 325°C. At 425°C lithium diffuses through 0.018" of silicon in 30 minutes, so in a 90 minute diffusion there is at least an hour where the lithium is diffusing into the junction and P region and another 1 or 2 hours of driving lithium into the junction and P region during redistribution. Lithium concentration profiles have been determined for eight hour diffusions at 325°C but shorter diffusions have not been made or evaluated

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(4) Chynoweth, A.G. and K. G. McKay, Op cit, p. 426.

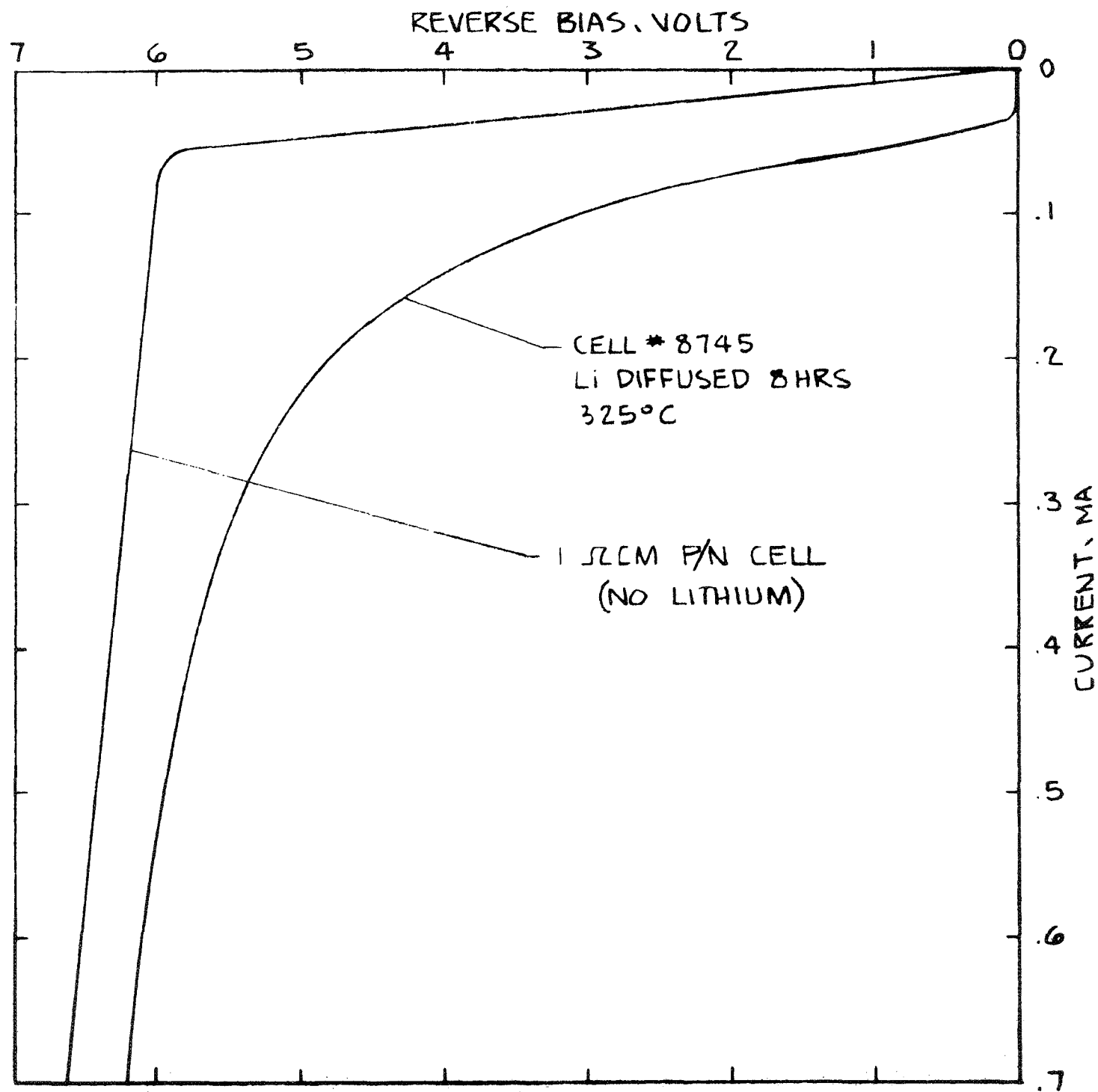


Figure 10. Comparison of Lithium Cell #8745 with Soft Reverse Characteristic to 1 ohm cm P/N Cell with Hard Reverse Characteristic.

and, consequently, both the length of time required to diffuse to the junction and the length of time lithium diffuses into the junction is unknown. Future work will include variations in the diffusion time at 325°C and this work may provide some insight into this problem. Working with a lower sodium content lithium source may also reduce the tunneling effect, since sodium has been known to be a very active impurity in semiconductor devices.

CONCLUSIONS

By reducing the boron deposition time the standard  $\text{BCl}_3$  diffusion (no  $\text{O}_2$ ) can be used to diffuse thin (0.004") and large area (2x6 cm) cells with no bowing.

In other experiments  $\text{BCl}_3$  diffusions with  $\text{O}_2$  have produced cells with outputs higher than 30 mW, which is equivalent to better than 11.3% efficiency. This is only 4 to 5% lower than typical cell efficiencies of cells diffused with the standard  $\text{BCl}_3$  diffusion (no  $\text{O}_2$ ). This diffusion process can also be used for large area cells since 2x6 cm blanks were not bowed. Silicon is not etched during the diffusion and, therefore, special cell types requiring a non-etching diffusion source can be made once the diffusion is optimized with respect to electrical output.

Typical efficiencies of 10.5 to 11.0% can be obtained with cells lithium diffused eight hours at 325°C; however, two problems have become apparent which cause lower efficiencies. These two problems have not been serious problems, since high outputs have been obtained; however, the spread in output could be reduced by eliminating the problems. One of the problems, a soft knee, can be eliminated by etching the cell edges. The other problem, tunneling or internal field emission, was found to occur not only in cells lithium diffused eight hours at 325°C, but also in varying degrees in cells with other lithium diffusion parameters and 1 ohm cm P/N cells with no lithium. However, only cells lithium diffused eight hours at 325°C exhibited the excessive current between 0 and 0.1 volt in reverse bias and the shunted characteristic in the forward direction when illuminated.